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Dipole moment studies of some ortho substituted benzaldehydes

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Abstract The ortho dipole effect of o-chloro, o-nitro, o-hydroxy and o-methoxy benzaldehydes in benzene and p-xylene solutions has been determined by comparing the observed dipole moment values and the dipole moment values calculated using group moments and bond angles. Using the dipole moment values corresponding to overall rotation and internal rotations (calculated from microwave dielectric data) for these molecules, the angle molecular dipole moment makes with the long axis of the molecule [carbon (1) - carbon (4) axis of benzene ring] have been evaluated. A method for determination of the change in the angle of the aldehyde group makes with its axis of rotation due to ortho substitution have been given using microwave data and it is applied in case of o-chloro and o-nitro benzaldehydes. The ortho dipole effect and solute solvent interactions has been discussed for molecular conformations of these molecules.

Keywords Dipole moments, ortho dipole effect, microwave group rotation data

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1. Introduction

Dipole moment studies are of great help in the assignment of the geometrical molecular structures or configurations, particularly those of organic compounds. These studies provide valuable information about the internal rotation in the molecule. There are several books [1-10] which deal with the theory of dipole moment and molecular structure. The electric dipole moment of a polar molecule can be determined from solution data, temperature variation of permittivity, refractivity method, microwave absorption in liquids, stark splitting, infrared absorption studies *etc.* Out of these methods the determination of dipole moment from solution data is most convenient and mainly used by the workers engaged in dielectric studies. The dipole moment of an isolated molecule can be accurately determined from the measurement of static permittivity of its vapour at different temperatures. The dipole moment evaluated in dilute solution of non-polar solvent is in reasonable agreement with its gaseous value, because of the fact that in dilute solution the system is in a quasi-isolated state and polar molecules are well separated

from one another and consequently the dipole-dipole interactions are absent. Solute-solvent interactions may cause variation in dipole moment from one solvent to another. This is termed as solvent effect. Dipole moment of the molecules can also be determined using bond moments and bond angles. In general, there is good agreement between the calculated and observed values of the dipole moment in aliphatic molecules and meta and para substituted aromatic molecules. In case of ortho disubstituted benzenes, the dipole moment values observed are consistently lower than those calculated. When one dipole has its positive end toward the ring and the other dipole with its positive end away from the ring the calculated values are lower than the observed values. This discrepancy between the observed and calculated values for the ortho compounds, is often called the 'ortho effect.'

In ortho disubstituted benzene, the intramolecular displacement of the electron distribution due to addition of polarizable groups is involved and is reflected in change in bonding conditions (inductive effect) and hence there is change in the angle that a group dipole makes with its axis of rotations. Using observed and calculated values of molecular dipole moments of the ortho disubstituted benzenes the ortho effect can be evaluated. If the observed values are available in different solvents then the solvent effect can also be determined and the nature of solute-solvent interactions can be predicted.

The main object of the present paper is to show the various changes developed in the geometrical molecular structures of ortho substituted benzaldehydes due to ortho effect with the help of earlier dipole studies and microwave data carried out in this laboratory.

2. Theory

In ortho disubstituted benzenes, if group rotations are absent *i.e.* the angles which the group moments make with their axes of rotation are zero, the molecular dipole moment can be determined using group moments by the equation

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta. \tag{1}$$

In case of internal group rotations, Fuchs [11] gave an equation for the determination of molecular dipole moment of ortho disubstituted benzenes *i.e.*

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta \cos\theta_1 \cos\theta_2, \tag{2}$$

where μ_1 and μ_2 are the group moments of the respective mono substituted benzenes in dilute solutions, θ is the angle between the axis of rotation of the groups in the disubstituted benzene *i.e.* equal to 60° for ortho isomers. θ_1 and θ_2 are the angles which the group moments make with their axes of rotation of the respective mono substituted benzenes in dilute solutions.

If only one rotatable group is there then the molecular dipole moment can be calculated by substituting either $\theta_1 = 0$ or $\theta_2 = 0$ in eq. (2). The molecules in which there are no internal rotations, $\theta_1 = \theta_2 = 0$, hence eq. (2) will reduce to general eq. (1).

The molecules which have only one rotatable group of either dipole moment μ_1 or μ_2, the dipole moment for internal rotation can be evaluated by

$$\mu_{\text{int.rot}} = \mu_1 \sin\theta_1' \tag{3a}$$

or

$$\mu_{\text{int.rot}} = \mu_2 \sin\theta_2', \tag{3b}$$

where θ_1' and θ_2' are the angles μ_1 and μ_2 make with their axes of rotation in ortho disubstituted benzenes *i.e.* the changed angles due to ortho effect.

The $\mu_{\text{int rot}}$ for these molecules can be evaluated using microwave dielectric data. If $\mu_{\text{int rot}}$ is known then the angles θ_1' and θ_2' can be evaluated as

$$\theta_1' = \sin^{-1}(\mu_{\text{int rot}} / \mu_1) \tag{4a}$$

or

$$\theta_2' = \sin^{-1}(\mu_{\text{int rot}} / \mu_2) \tag{4b}$$

and therefore the change in the angles of μ_1 or μ_2 due to ortho effect can be determined as

$$\Delta\theta_1 = \theta_1 - \theta_1' \tag{5a}$$

and

$$\Delta\theta_2 = \theta_2 - \theta_2' \tag{5b}$$

For the molecules having both rotatable groups, determination of the individual displacement of the angles of the group moment from their axes of rotation is not possible.

3. Calculations and discussion

The molecular dipole moment of o-chloro, o-nitro, o-hydroxy and o-methoxy benzaldehydes have been calculated using eq. (2). These are reported in Table 1. The literature value [1] of the group moments and the angles which the group moments make with their axes of rotation of the mono substituted benzenes in dilute solutions have been used for the calculation of molecular dipole moment. The observed dipole moment μ_{obs} [12, 13] of these molecules in dilute solutions of benzene and p-xylene [Table 1] determined earlier in this laboratory have been used for determination of ortho dipole effect. Except o-methoxy benzaldehyde it has been observed that for these molecules the μ_{obs} values are lower than the μ_{cal} values in both the solvents. These discrepancies in μ values $\Delta\mu = \mu_{\text{cal}} - \mu_{\text{obs}}$ are listed in Table 1. $\Delta\mu$ values represent the ortho dipole effect in these molecules. This can be attributed to widening of the angle between the two dipole axes by steric repulsion between the two groups. It is inferred that the ortho dipole effect in ortho substituted benzaldehydes depends on the values of the dipole moment of ortho substituted groups. It is larger for o-nitro benzaldehyde because nitro group have large value of dipole moment [3.98 D] in comparison to the chloro [1.58 D] and hydroxy [1.6 D]. The observed dipole moment values for o-dichloro benzene [1] in dilute solution were also reported to be 1/3 times lower than the calculated values. For o-methoxy benzaldehydes μ_{obs} is higher than the μ_{cal}. This is owing to the opposite directions of the group dipoles *i.e.* one dipole is

Table 1. Values of dipole moments/D and ortho dipole effect of ortho substituted benzaldehydes

Molecules	μ_{obs}		μ_{cal}	$\Delta\mu = \mu_{\text{cal}} - \mu_{\text{obs}}$		$\Delta\mu' = A - B$
	A	B		A	B	
o-chloro benzaldehyde	3.17	3.20	3.55	0.38	0.35	0.03
o-nitro benzaldehyde	4.57	4.48	5.45	0.88	0.97	0.09
o-hydroxy benzaldehyde	2.96	2.86	3.37	0.41	0.51	0.10
o-methoxy benzaldehyde	4.70	4.34	3.21	1.49	1.31	0.36

directed towards the ring while the other is away from it. Ortho effect in o-hydroxy benzaldehyde is very large in comparison to the other molecules which may be also due to the opposite directions of the disubstituted groups from benzene ring. These discrepancies in the μ_{obs} and μ_{cal} values can be understood by inductive effect.

The discrepancies $\Delta\mu'$ in the dipole moment values of these molecules in benzene and p-xylene solutions are listed in Table 1. For o-chloro, o-nitro and o-hydroxy benzaldehydes, the change is very small which suggests that the solute-solvent interactions in benzene and p-xylene are of similar nature. Earlier [12-15] microwave relaxation measurements established the fact that these solvents have similar characteristics in so far as the interactions with benzaldehydes are concerned and are fairly weak. However in case of o-methoxy benzaldehyde the change in μ_{obs} value in these solvents is appreciable (= 0.36 D). This indicates that the characteristics of solute-solvent interactions in benzene and p-xylene differ sufficiently when one dipole is directed towards the ring and the other away from it.

Earlier [13] in this laboratory, microwave dielectric dispersion curves of o-chloro and o-methoxy benzaldehydes were resolved into two distinct Debye type curves corresponding to overall rotation of the molecule and group rotations. From these curves the dipole moments corresponding to overall rotation $\mu_{over\ rot}$ and internal rotations $\mu_{int\ rot}$ (group rotations) were determined. These are listed in Table 2. In case of o-hydroxy and o-nitro benzaldehydes, the microwave dielectric dispersion curves [12] could not be resolved into two distinct Debye type curves. For these molecules $\mu_{int\ rot}$ values have been estimated by Singh and Vij [14] method which is based on Higasi [16] equation using microwave dielectric data and are reported in Table 2. Using the μ_{obs} and $\mu_{int\ rot}$ values, $\mu_{over\ rot}$ has been determined from these molecules by the equation

$$(\mu_{obs})^2 = (\mu_{int\ rot})^2 + (\mu_{over\ rot})^2. \tag{6}$$

Table 2. Values of dipole moments/D corresponding to overall rotation and internal rotations and angles α, θ_i' and $\Delta\theta_i$

Molecules	$\mu_{over\ rot}$		$\mu_{int\ rot}$		α		θ_i'		$\Delta\theta_i=\theta_i-\theta_i'$	
	A	B	A	B	A	B	A	B	A	B
o-chloro benzaldehyde	2.48	2.45	1.97	2.04	38.5	39.8	45.5	47.7	9.5	7.3
o-nitro benzaldehyde	4.28	4.11	1.61	1.77	20.6	23.3	35.7	39.9	19.9	15.1
o-methoxy benzaldehyde	3.73	3.50	2.86	2.56	37.5	36.1				
o-hydroxy benzaldehyde	2.53	2.62	1.53	1.15	31.1	23.7				

In Tables, A and B represent the values in benzene and p-xylene solutions respectively.

Grubb and Smyth [17] showed that the angle α, that the molecular dipole moment substends with the long axis of the molecule [between the carbon (1) – carbon (4) axis in the benzene ring] can be evaluated by the equations

$$\mu_{int\ rot} = \mu_{obs} \sin\alpha \tag{7a}$$

or

$$\mu_{over\ rot} = \mu_{obs} \cos\alpha . \tag{7b}$$

Substituting the values of $\mu_{int\ rot}$ and μ_{obs} in the above eq. (7), the angle has been evaluated for these molecules in both the solvents and are reported in Table 2.

When the alone –CHO group is attached to the benzene ring, the – CHO dipole makes an angle of 55° with the C–C bond [1]. The addition of polar group in the ortho position of the benzaldehyde leads to a change in the angle which the dipole of the –CHO group makes with the C–C bond. From the structural considerations of o-chloro and o-nitro benzaldehydes alone, one would not expect any dipole moment contribution for the internal rotations from the chloro and nitro groups. This is because rotations of the chloro and the nitro group along their respective bonds to the carbon atom of the molecule do not give rise to a change in the direction of the group dipole moment. Hence the $\mu_{int\ rot}$ values for these molecules are only due to the rotation of –CHO group along the C-C bond axes. Using eq. (5), the changed angle of –CHO group θ_1' due to substitution of chloro and nitro groups at ortho position have been determined in both the solvents and are reported in Table 2. It is observed that the change in the angle of –CHO group in case of o-nitro benzaldehyde is large in comparison to the o-chloro benzaldehyde. This is expected because of the higher value of dipole moment of nitro group in comparison to the chloro group. The calculated value of the –CHO angle in case of o-nitro benzaldehyde is fairly in agreement with the earlier [18] reported value *i.e.* 36.5°. In case of o-methoxy and o-hydroxy benzaldehydes, the rotations of methoxy and hydroxy groups along their respective axis gives rise to a change in the direction of the group dipole moments so they contribute to the values of $\mu_{int\ rot}$. Therefore for these molecules, $\mu_{int\ rot}$ values are due to combined effect of the rotation of both the groups and hence it is not possible to evaluate the values of the changed angles of individual groups.

4. Conclusions

The ortho dipole effect and the solvent effect on molecular dipole moment can be found for other ortho-disubstituted benzene molecules in the same way as described in this paper. Further, the method of detection of the effect on moment angle of rotatable group due to the other group which is not contributing to the dipole moment for internal rotations, presented here is simple and may be applied for similar molecules. The angle of resultant molecular dipole moment makes with the long axis of the molecule [carbon (1) – carbon (4) axis of the benzene ring] can also be made for other o-disubstituted benzene molecules using the technique given in this manuscript. All these aforesaid effects can be calculated if the $\mu_{int\ rot}$ values observed using microwave dielectric data or by other techniques are available. These values are very helpful in the determination of geometrical structures of such organic molecules.

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